NANOLAYER THICK FILM PROCESSING
SYSTEM AND METHOD

Inventors

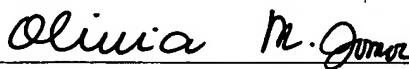### TUE NGUYEN
TAI DUNG NGUYEN

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NANOLAYER THICK FILM PROCESSING SYSTEM AND METHOD

INVENTORS: TUE NGUYEN and TAI DUNG NGUYEN

This Application is a Continuation of Application No. 09/954,244 filed on

September 10, 2001, entitled: "Nanolayer Thick Film Processing System and Method."

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BACKGROUND

The present invention relates to semiconductor thin film processing by nanolayer

deposition ("NLD"). The fabrication of modern semiconductor device structures has

traditionally relied on plasma processing in a variety of operations such as etching and

20   deposition. Plasma etching involves using chemically active atoms or energetic ions to

remove material from a substrate. Deposition techniques employing plasma includes

Chemical Vapor Deposition ("CVD") and Physical Vapor Deposition ("PVD") or

sputtering.

PVD uses a high vacuum apparatus and generated plasma that sputters atoms or

25   clusters of atoms toward the surface of the wafer substrates. PVD is a line-of-sight

5   deposition process that is more difficult to achieve conformal film deposition over

complex topography, such as deposition of a thin and uniform liner or barrier layer over

the small trench or via of 0.13 µm or less, especially with high aspect ratio greater than

4:1.

In CVD, a gas or vapor mixture is flowed over the wafer surface at an elevated

10   temperature. Reactions then take place at the hot surface where deposition takes place.

Temperature of the wafer surface is an important factor in CVD deposition, as it depends

on the chemistry of the precursor for deposition and affects the uniformity of deposition

over the large wafer surface. The high temperatures typically required for CVD

deposition may not be compatible with other processes in the semiconductor process.

15   Moreover, CVD at lower temperature tends to produce low quality films in term of

uniformity and impurities. More details on PVD and CVD are discussed in International

Pub. Number WO 00/79019 A1 or PCT/US00/17202 to Gadgil, the content of which is

incorporated by reference.

In atomic layer deposition ("ALD"), various gases are injected into a chamber for

20   as short as 100-500 milliseconds in alternating sequences. For example, a first gas is

delivered into the chamber for about 500 milliseconds and the substrate is heated, then

the first gas (heat optional) is turned off. Another gas is delivered into the chamber for

another 500 milliseconds (heat optional) before the gas is turned off. The next gas is

delivered for about 500 milliseconds (and optionally heated) before it is turned off. This

25   sequence is repeated until all gases have been cycled through the chamber, each gas

sequence forming a highly conformal monolayer. ALD technology thus pulses gas

injection and heating sequences that are between 100 and 500 milliseconds.

5   The ALD approach requires a high dissociation energy to break the bonds in the

various precursor gases, which can be, for example, silane and oxygen. ALD thus

requires high substrate temperature, for example, on the order of 600-800 degrees Celsius

for silane and oxygen processes.

United States Patent No. 5,916,365 to Sherman, entitled "Sequential chemical

10   vapor deposition" provides for sequential chemical vapor deposition by employing a

reactor operated at low pressure, a pump to remove excess reactants, and a line to

introduce gas into the reactor through a valve. Sherman teaches exposing the part to be

coated to a gaseous first reactant, including a non-semiconductor element of the thin film

to be formed, wherein the first reactant adsorbs on the part to be coated. The Sherman

15   process produces sub-monolayers as a result of adsorption. The first reactant forms a

monolayer on the part to be coated (after multiple cycles), while the second reactant

passes through a radical generator which partially decomposes or activates the second

reactant into a gaseous radical before it impinges on the monolayer. This second reactant

does not necessarily form a monolayer, but is available to react with the monolayer. A

20   pump removes the excess second reactant and reaction products completing the process

cycle. The process cycle can be repeated to grow the desired thickness of film.

United States Patent 6,200,893 to Sneh entitled "Radical-assisted sequential

CVD" discusses a method for CVD deposition on a substrate wherein radical species are

used in alternate steps to depositions from a molecular precursor to treat the material

25   deposited from the molecular precursor and to prepare the substrate surface with a

reactive chemical in preparation for the next molecular precursor step. By repetitive

cycles, a composite integrated film is produced. In a preferred embodiment, the

5   depositions from the molecular precursor are metals, and the radicals in the alternate

steps are used to remove ligands remaining from the metal precursor reactions, and to

oxidize or form a nitride of the metal surface in subsequent layers.

In one embodiment taught by Sneh, a metal is deposited on a substrate surface in

a deposition chamber by: (a) depositing a monolayer of metal on the substrate surface by

10   flowing a molecular precursor gas or vapor bearing the metal over a surface of the

substrate, the surface saturated by a first reactive species with which the precursor will

react by depositing the metal and forming reaction product, leaving a metal surface

covered with ligands from the metal precursor and therefore not further reactive with the

precursor; (b) terminating flow of the precursor gas or vapor; (c) purging the precursor

15   with inert gas; (d) flowing at least one radical species into the chamber and over the

surface, the radical species highly reactive with the surface ligands of the metal precursor

layer and eliminating the ligands as reaction product, and also saturating the surface,

providing the first reactive species; and (e) repeating the steps in order until a metallic

film of desired thickness is achieved.

20   In another aspect of the Sneh disclosure, a metal nitride is deposited on a substrate

surface in a deposition chamber by: (a) depositing a monolayer of metal on the substrate

surface by flowing a metal precursor gas or vapor bearing the metal over a surface of the

substrate, the surface saturated by a first reactive species with which the precursor reacts

by depositing the metal and forming reaction product, leaving a metal surface covered

25   with ligands from the metal precursor and therefore not further reactive with the

precursor; (b) terminating flow of the precursor gas or vapor; (c) purging the precursor

with inert gas; (d) flowing a first radical species into the chamber and over the surface,

5   the atomic species highly reactive with the surface ligands of the metal precursor layer

and eliminating the ligands as reaction product and also saturating the surface; (e)

flowing radical nitrogen into the chamber to combine with the metal monolayer deposited

in step (a), forming a nitride of the metal; (f) flowing a third radical species into the

chamber terminating the surface with the first reactive species in preparation for a next

10   metal deposition step; and (g) repeating the steps in order until a composite film of

desired thickness results.

The Sneh embodiments thus deposit monolayers, one at a time. Because the

objective is to create a thick film, the Sneh process is relatively time-consuming.

Atomic layer deposition (ALD or ALCVD) is a modified CVD process that is

15   temperature-sensitive and flux-independent. ALD is based on a self-limiting surface

reaction. ALD provides a uniform deposition over complex topography and is

temperature-independent, since the gases are adsorbed onto the surface. ALD can occur

at lower temperature than CVD, because ALD is an adsorption regime.

As discussed in connection with the Sherman and Sneh patents, above, the ALD

20   process includes cycles of flowing gas reactant into a chamber, adsorbing one sub-

monolayer onto the wafer surface, purging the gas reactant, flowing a second gas reactant

into the chamber, and reacting the second gas reactant with the first gas reactant to form a

monolayer on the wafer substrate. Thick film is achieved by deposition of multiple

cycles.

25   Precise thickness can be controlled by number of cycles, since a single monolayer

is deposited as a result of each cycle. However, the conventional ALD method is a slow

process to deposit films such as those around 100 angstroms in thickness. Growth rate of

5   Atomic Layer Epitaxy ("ALE") TiN for example was reported at 0.2 angstrom/cycle,

which is typical of metal nitrides from corresponding chlorides and NH_3.

The throughput in device fabrication for a conventional ALD system is slow.

Even if the chamber is designed with minimal volume, the throughput is still slow due to

the high number of cycles required to achieve the desired thickness. Conventional ALD

10   is a slower process than CVD, with ALD having a rate of deposition almost 10 times

slower than CVD. The process is also chemical-dependent; that is, it is necessary to

ensure the proper self-limiting surface reaction for deposition.

5

SUMMARY

In one aspect, a nano-layer deposition ("NLD") process of depositing a thin film by chemical vapor deposition includes evacuating a chamber of gases; exposing a device to a gaseous first reactant, wherein the first reactant deposits on the device to form the

10   thin film; evacuating the chamber of gases; and exposing the device, coated with the first reactant, to a gaseous second reactant under plasma, wherein the thin film deposited by the first reactant is treated to form the same materials or a different material.

Embodiments of the present invention can include one or more of the following. The device can be a wafer. The plasma either can enhance or maintain the thin film

15   conformality. The plasma can be a high density plasma with density exceeding 5×10^9 ion/cm^3. The reactant can be a metal organic, organic, to form a thin film of metal, metal nitride, or metal oxide. The second reactant is exposed under pressure, above 100 mT. The first and second reactants react and the reaction creates a new compound. The thin film thickness is more than one atomic layer in thickness. The thin film thickness can be

20   between a fraction of a nanometer and tens of nanometers. The plasma can be sequentially pulsed for each layer to be deposited. The plasma can be excited with a solid state radio frequence ("RF") plasma source, such as a helical ribbon electrode. The chamber containing the device can be purged.

The process includes pre-cleaning a surface of a device; evacuating a chamber;

25   stabilizing precursor flow and pressure; exposing the device to a first reactant, wherein the first reactant deposits on the device to form the nanolayer thin film having a thickness of more than one atomic layer; purging the chamber; evacuating the chamber; striking the

5   plasma; performing a plasma treatment on the deposited film; exposing the device, coated

with the first reactant, to a gaseous second reactant under the plasma treatment, wherein

the thin film deposited by the first reactant is treated to form the same materials or a

different material. Repeating the above cycle deposits a thick film, where the thickness is

determined by the number of times the cycle is repeated.

10   In another aspect, the deposition steps discussed above can take place in multiple

chambers. The process includes pre-cleaning of the device surface; evacuating the

chamber; stabilizing precursor flow and pressure; exposing the device to a first reactant,

wherein the first reactant deposits on the device to form the nanolayer thin film having a

thickness of more than one atomic layer; purging the chamber; and, evacuating the

15   chamber. The device then is transferred to another chamber that is purged and pumped.

The next step is striking the plasma, followed by performing a plasma treatment on the

deposited film; exposing the device, coated with the first reactant in the first chamber, to

a gaseous second reactant under the plasma treatment in the second chamber, wherein the

thin film deposited by the first reactant is treated to form the same materials or a different

20   material. Repetition of this cycle in the first and second chambers deposits a thick film,

wherein the thickness of the resulting film depends upon the number of cycles of

repetitions.

In another aspect of the invention, an apparatus to perform semiconductor

processing includes a high density inductively-coupled plasma source enclosed in a

25   process chamber, wherein a device is exposed inside the chamber to a gaseous first

reactant. The first reactant deposits on the device to form a thin film. After purging, the

device, coated with the first reactant, is exposed to a gaseous second reactant under

5 plasma, wherein the thin film deposited by the first reactant is treated to form the same

materials or a different material. The method can provide deposition of copper metal

from Cu hfacI and plasma (gas), Cu hfacII and plasma (gas), CuI_4 and plasma (gas),

$CuCl_4$ and plasma (gas), and organo metallic and plasma (gas); of titanium nitride from

tetrakisdimethyl titanium ("TDMAT") and plasma (gas), tetrakisdiethyl titanium

10 ("TDEAT") and plasma (gas), tetrakis (methylethylamino) titanium ("TMEAT") and

plasma (gas), $TiCl_4$ and plasma (gas), TiI_4 and plasma (gas), and organo metallic and

plasma (gas); of tantalum nitride from penta-dimethyl-amino-tantalum ("PDMAT") and

plasma (gas), pentakis(diethylamido)tantalum ("PDEAT") and plasma (gas), and organo

metallic and plasma (gas); wherein gas is one of N_2, H_2, Ar, He, NH_3, and combination

15 thereof.

Implementations of the apparatus can include gas distribution, chuck, vaporizer,

pumping port to pump, and port for gas purge.

Advantages of the system may include one or more of the following. The

resulting deposition is highly conformal and is similar in quality to that of ALD. The

20 nanolayer thick film deposition process provides almost 100 % conformal deposition on

complex topography as that in semiconductor devices having 0.1 micron width with an

aspect ratio greater than 8:1. Excellent conformality of film is achieved with NLD

similar to that of ALD, and far superior than conformality of thick CVD film. Further,

such conformality is achieved rapidly, since multiple atomic layers up to a few

25 nanometers thick are deposited as a result of each cycle of NLD. In contrast, ALD

processes only one wafer at a time, requires a small volume, deposits only one monolayer

at a time. The advantage of NLD over ALD thus is higher throughput over ALD.

5   The microstructure of the film resulting from NLD can be of a nanocrystalline

grain structure in an amorphous matrix using the NLD technique, since a film of more

than a monolayer to a few nanometer thick is deposited in each cycle. This structure is

not typical of conventional CVD or PVD. The surface morphology of the films deposited

by NLD is also smoother than that of films deposited by conventional CVD. This

10   microstructure and morphology can be ideal for certain applications. In the application of

copper diffusion barrier thin film deposition, this microstructure of the barrier thin film is

a key to the resistance to copper. In fact, our initial data show that our NLD TiN film

deposited from TDMAT precursor and N_2 plasma has superior barrier properties to PVD

TiN, PVD TaN, or conventional CVD TiN. Additionally, the low temperature of the

15   NLD deposition process, which can be lower than that of CVD, is consistent with the

processing requirements of advanced films, such as low-k dielectric.

The precursors or gases usable in the NLD process are not limited to those having

the self-limiting surface reactions, since NLD is a deposition process. NLD thus employs

a much broader spectrum of precursors and can be used to deposit a vast number of film

20   materials from a variety of available precursors. Since NLD has high throughput,

minizing the chamber volume, as is necessary in ALD, is not necessary. Consequently, a

conventional CVD chamber can be used to achieve highly conformal, high quality, high

throughput films.

Other advantages of the system may include one or more of the following. The

25   helical ribbon provides a highly uniform plasma which does not require a chamber with a

small volume. The system enables high precision etching, deposition, or sputtering

performance. This is achieved using the pulse modulation of a radio frequency-powered

5   plasma source, which enables a tight control over the radical production ratio in plasmas, the ion temperature, and charge accumulation. Also, since the time for accumulation of charges in a wafer is on the order of milli-seconds, the accumulation of charges to the wafer is suppressed by the pulse-modulated plasma on the order of micro-seconds, and this enables the suppression of damage to devices on the wafer caused by the charge

10   accumulation and of notches caused during the electrode etching process. The system requires that the substrate be heated to a relatively low temperature, such as 400 degrees Celsius.

Yet other advantages may include one or more of the following. The system attains highly efficient plasma operation in a compact substrate process module that can

15   attain excellent characteristics for etching, depositing or sputtering of semiconductor wafers, as represented by high etch rate, high uniformity, high selectivity, high anisotropy, and low damage. The system achieves high density and highly uniform plasma operation at low pressure for etching substrates and for deposition of films on to substrates. Additionally, the system is capable of operating with a wide variety of gases

20   and combinations of gases, including highly reactive and corrosive gases.

5

BRIEF DESCRIPTION OF THE DRAWINGS

Figs. 1A-1E show exemplary embodiments of a plasma processing system with a helical ribbon.

Figs. 2A-2C show more details of the helical ribbon of Fig. 1.

10 Fig. 3 shows a flowchart of one exemplary semiconductor manufacturing process using the system of Fig. 1.

Figs. 4A-4B show exemplary generator embodiments.

Fig. 5 shows a multi-chamber semiconductor processing system.

Fig. 6 shows a diagram of an exemplary apparatus for liquid and vapor precursor

15 delivery.

Figs. 7A-7B show two operating conditions of an embodiment to perform plasma deposition.

Fig. 8 shows a flow chart of a nanolayer thick film process in accordance with one embodiment of the invention.

20 Fig. 9 shows an SEM of an exemplary wafer created in accordance with one embodiment of the invention.

Fig. 10 shows a plot of film resistance increase as a function of time for an exemplary process recipe.

DESCRIPTION

Fig. 1A shows an exemplary plasma processing system 100 with a processing

chamber 102. The process chamber 102 has a chamber body enclosing components of

the process chamber such as a chuck 103 supporting a substrate 105. The process

chamber typically maintains vacuum and provides a sealed environment for process gases

during substrate processing. The process chamber periodically must be accessed to

cleanse the chamber. An opening typically is provided for maintenance at the top of the

process chamber that is sufficiently large to provide access to its the internal components.

The chamber 102 includes a plasma excitation circuit 106 driven by a solid-state

plasma generator 110 with fast ignition capability. One commercially available plasma

source is the Litmas source, available from LITMAS Worldwide of Matthews, North

Carolina. The generator 110 includes a switching power supply 112 that is connected to

an alternating current (AC) line. The power supply 112 rectifies AC input and switches

the AC input to drive an RF amplifier 116. The RF amplifier 116 operates at a reference

frequency (13.56 MHz, for example) provided by a reference frequency generator 104.

The RF amplifier 116 drives current through a power measurement circuit 118 that

provides feedback signals to a comparator 120 and to the reference frequency generator

104. In this embodiment, power is measured only once, and the information is used to

control the RF amplifier 116 gain, as well as a tuning system if needed. Power is then

delivered to an output match section 122, which directly drives the plasma excitation

circuit 106. In one embodiment (Fig. 1C), the plasma excitation circuit 106 uses helical

ribbon electrodes 170 in the chamber. However, other equivalent circuits can be used,

5   including (Fig. 1B) an external electrode of capacitance coupling or inductance coupling type, for example.

Positioned above the helical ribbon electrodes 170 is a heat exchanger 182 that removes heat from the helical ribbon electrodes 170 during operation. In one embodiment, the heat exchanger is a pipe that circulates fluid to remove heat. The fluid

10   moves through the pipe and the helical ribbon electrodes 170. Fluid then enters the heat exchanger 182 and traverses through a loop. Thermal energy in the form of heat transfers to fluid in another loop, which is cooler in temperature and draws heat away from the heat in the fluid in the first loop. In a specific embodiment, cooling fluid enters and leaves the heat exchanger 182.

15   A controller 130 generates a periodic pulse and drives one input of the frequency reference 104. The pulse effectively turns on or off the plasma generation. One embodiment of the controller 130 generates a pulse with a frequency of ten hertz (10Hz) or less. In another embodiment, the pulse generated has a pulse-width of approximately two hundred fifty (110) millisecond and the pulse is repeated approximately every fifty

20   (50) microseconds.

Turning now to Fig. 1B, a second embodiment is shown. Fig. 1B includes a helical ribbon electrode 170 connected to a generator 110. The helical ribbon electrode 170 rests above a dielectric wall 154. The dielectric wall 154 rests above a chamber 102 and is supported by chamber walls 158. The dielectric wall 154 allows the energy

25   generated from the generator 110 to pass through to generate a plasma inside the chamber 102. The dielectric materials can be any non-metallic materials such as ceramic, glass, quartz, or plastic.

5   Fig. 1C shows a third embodiment where the helical ribbon electrode 170 is

positioned inside a chamber 102 with walls 158. The walls 158 have an electrical feed

through 155, through which the generator 110 can drive the helical ribbon electrode 170.

There need not be a dialectric plate 154.

Fig. 1D shows a fourth embodiment where the helical ribbon electrode 170 wraps

10   around a tubular dielectric wall 154. A chamber 102 is positioned within the helical

ribbon electrode 170 and the tubular dielectric wall 154, through which the generator 110

can drive the helical ribbon electrode 170.

Fig. 1E shows a fifth embodiment optimized for pulsed processing. This

embodiment has a helical ribbon electrode 170 connected to a generator, with the helical

15   ribbon resting above a dialectric wall 154. This embodiment further has an elongated

chamber 102 with a small volume 186 above a wafer 183. The volume is dependent on

the diameter of the wafer 183 and the distance between the helical ribbon electrode 170

and the wafer. Typically, the distance is less than five (5) inches, but can also be between

one and three inches. The helical ribbon electrode 170 in turn is driven by the generator

20   110. The large ratio of the width to the thickness of the helical ribbon electrode allows

the short distance and still offers the plasma uniformity required on the wafer surface.

The characteristics of a film deposited by the above techniques depend upon the

electron temperature in the plasma, the energy of ion incident on a substrate, and the ions

and radicals produced in the vicinity of an ion sheath. The electron temperature

25   distribution in the plasma, the kinds of ions and radicals produced in the plasma, and the

ratio between the amount of ions and radicals, can be controlled by modulating a high-

frequency voltage in the same manner explained with respect to plasma etching.

5   Accordingly, when conditions for depositing a high quality film are known, the discharge

plasma is controlled by a modulated signal according to the present invention, so that the

above conditions are satisfied. Thus, the processing characteristics with respect to film

deposition can be improved.

Figs. 2A-2C show more details of the helical ribbon electrode 170. In Fig. 2A, an

10   elongate conductive coil 172 insulated by a sheet of dielectric material 174 is wound to

form a cylindrical helix. The two sides of the helix are then compressed into planes such

that the coil 172 surfaces in each side lie flat and engage the adjacent side of the sheet of

dielectric material 174.

The ribbon coil 172 can have about three to ten turns and can be made of any

15   conductive, ductile metal, such as copper or aluminum. The coil 172 has a width that is

substantially greater than its thickness. Preferably, the width is approximately one

hundred times the thickness, although the ratio of width w to thickness t may conceivably

range from 1 to 10000, depending on mechanical considerations and/or electrical

parameters. Mechanical considerations affecting the optimum width:thickness ratio

20   include, for example, build height and turns ratio. In one embodiment, the coil 172 can

have three turns, with the width of the coil 172 at about 40 millimeters and a thickness at

about one millimeter.

Electrical parameters affecting the optimum width:thickness ratio include, for

example, electrical resistance, skin effect, and proximity effect. During manufacturing,

25   the conductive coil 172 and dielectric sheet 174 are wound in one continuous direction on

a cylindrical mandrel and then compressed into a plane. With the exception of the

outermost coil layers, the compressed coil engages on one side a sheet of dielectric

5 material, and on the other side a sheet of dielectric material. Bends (not shown) are

formed in the ribbon coil 172 near the ends so that the ends project radially from

conductive coil 172 for external connection.

The conductive coil 172 is then compressed into a pancake with multiple layers

such that the coils lie flat and engage one side of the dielectric material sheet 174. The

10 compressed sides form a flat coil. The width of the conductive coil 172 is less than the

width of the dielectric material sheet 174 such that, when compressed, the interior or

exterior of adjacent coil surfaces do not touch. The ends of the ribbon coil 172 project

from the outer coil surfaces, where they can be attached to other electrical components.

The coil 172 can be adhered to sheet 174 of dielectric material by at least two

15 methods. One method is to provide a sheet of dielectric material that is coated on both

sides with thermal-set adhesive. After compression, a winder is heated sufficiently to

activate the thermal-set adhesive to adhere the coil 172 to the dielectric material sheet

174. A second method is to adhere the coil 172 to sheet 174 by insulating adhesive tape

disposed between each coil layer. In one embodiment, the helical ribbon electrode 170 is

20 available from LITMAS Corporation of Matthews, North Carolina.

The helical ribbon electrode 170 enhances the uniformity of power density due to

its width:thickness ratio. Power transmittance is higher because the helical ribbon

electrode 170 is closer to the chamber. The result is reduced power loss. The helical

ribbon electrode 170 is low in profile, and supports a high density, low profile

25 semiconductor processing system.

Fig. 3 shows a flowchart of one exemplary semiconductor manufacturing process

using the system 100 of Fig. 1. First, a wafer is positioned inside the chamber (step 200).

5   Next, suitable processing gas is introduced into the chamber (step 202). The chamber is

pressurized to a pressure level such as four hundred millitorr (400mT). The pressure

level can range between about one hundred millitorr (100mT) to about ten torr (10T)

(step 203). The controller 130 (depicted in Fig. 1A) is turned on periodically, in

accordance with a process activation switch to drive the desired process (step 204). The

10   particular type of process to be performed affects the process activation switch choice.

The choice of activation switch for any device fabrication process, regardless of whether

the process is a deposition or etch process, also may significantly affect the final

semiconductor device properties. At the conclusion of the processing of one layer of

material, the gas in the chamber is purged (step 206), and the chamber is ready to accept

15   further processing. For the next layer of material, suitable processing gas is introduced

into the chamber (step 208). The chamber is pressurized to a pressure level above

approximately one hundred millitorr (100mT), and the controller 130 is periodically

turned on to drive the desired process (step 210). At the conclusion of the processing of

the second layer of material, the gas in the chamber is purged (step 212), and the chamber

20   is ready to accept another processing gas to process and deposit another layer of material.

This process is repeated for each layer in the multi-layer film.

In another embodiment, thin film is deposited using chemical vapor deposition by

evacuating a chamber of gases; exposing a part to be coated to a gaseous first reactant,

wherein the first reactant deposits on the part to form the thin film; evacuating the

25   chamber of gases; exposing the part, coated with the first reactant, to a gaseous second

reactant of plasma at a high pressure, wherein the plasma converts the second reactant on

5   the part to one or more elements, wherein the thin film deposited is treated; and,

evacuating the chamber of gases.

Fig. 4A shows one exemplary controller 130. The controller 130 includes a

computer 131 driving a digital to analog converter ("DAC") 133. The DAC 133

generates shaped waveforms and is connected to a high-voltage isolation unit 135 such as

10   a power transistor or a relay to drive the plasma generator 110. The controller 130 can

generate various waveforms such as a rectangular wave and a sinusoidal wave, and

moreover can change the period and amplitude of such waveforms. Further, in the above

explanation, the RF power supplied to a plasma is modulated with a rectangular wave.

The modulation wave form is determined in accordance with known factors, including: a

15   desired ion energy distribution; a desired electron temperature distribution; and a desired

ratio between the amount of the desired ion and the amount of the desired radical. The

use of a rectangular wave as the modulation waveform is advantageous because a

processing condition can be readily set and the plasma processing can be readily

controlled. It is to be noted that since the rectangular wave modulates the signal from

20   the RF source in a discrete fashion, the rectangular wave can readily set the processing

condition, as compared with the sinusoidal wave and the compound wave of it. Further,

the pulse generator can also generate amplitude-modulated signals in addition, or in

combination with, the frequency-modulated signals.

Fig. 4B shows an exemplary embodiment that uses a timer chip such as a 137

25   timer, available from Signetics of Sunnyvale, CA. The timer chip 137 is preconfigured

through suitable resistive-capacitive ("RC") network to generate pulses at specified

intervals. The timer chip 137 generates shaped waveforms and is connected to a high-

5   voltage isolation unit 135, such as a power transistor or a relay, to drive the plasma

generator 110 (as in Fig. 1A), as discussed above.

Referring now to Fig. 5, a multi-chamber semiconductor processing system 300 is

shown. The processing system 300 has a plurality of chambers 302, 304, 306, 308 and

310 adapted to receive and process wafers. Controllers 322, 324, 326, 328 and 330

10   control each of the chambers 302, 304, 308 and 310, respectively. Additionally, a

controller 321 controls another chamber, which is not shown.

Each of chambers 302, 304, 306, 308, 310 has a lid over each chamber body.

During maintenance operations, the lid can be actuated into an open position so that

components inside the chamber bodies can readily be accessed for cleaning or

15   replacement as needed.

The chambers 302, 304, 306, 308, 310 are connected to a transfer chamber (not

visible) that receives a wafer. The wafer rests on top of a robot blade or arm (not

depicted). The robot blade receives wafer from an outside processing area.

The transport of wafers between processing areas entails passing the wafers

20   through one or more doors separating the areas. The doors can be load lock chambers

360, 362 for passing a wafer-containing container or wafer boat that can hold about

twenty-five wafers in one embodiment. The wafers are transported in the container

through the chamber from one area to another area. The load lock can also provide an air

circulation and filtration system that effectively flushes the ambient air surrounding the

25   wafers.

Each load lock chamber 360, 362 is positioned between sealed opening (not

visible), and provides the ability to transfer semiconductor wafers between fabrication

5   areas. The load locks 360, 362 can include an air circulation and filtration system that

effectively flushes the ambient air surrounding the wafers. The air within each load lock

chamber 360, 362 can also be purged during wafer transfer operations, significantly

reducing the number of airborne contaminants transferred from one fabrication area into

the other. The load lock chambers 360, 362 can also include pressure sensors that take

10   air pressure measurements for control purposes.

During operation, a wafer cassette on a wafer boat is loaded at openings in front

of the system to a load lock through the load lock doors. The doors are closed, and the

system is evacuated to a pressure as measured by the pressure sensors. A slit valve (not

shown) is opened to allow the wafer to be transported from the load lock into the transfer

15   chamber. The robot blade takes the wafer and delivers the wafer to an appropriate

chamber. A second slit valve opens between the transfer chamber and process chamber,

and wafer is brought inside the process chamber.

Containers thus remain within their respective fabrication areas during wafer

transfer operations, and any contaminants clinging to containers are not transferred with

20   the wafers from one fabrication area into the other. In addition, the air within the transfer

chamber can be purged during wafer transfer operations, significantly reducing the

number of airborne contaminants transferred from one fabrication area into the other.

Thus during operation, the transfer chamber provides a high level of isolation between

fabrication stations.

25   Fig. 6 shows an exemplary apparatus 400 for liquid and vapor precursor delivery

using system 100. The apparatus 400 includes a chamber 402 that can be a CVD or NLD

chamber. The chamber 402 includes a chamber body 458 that defines an evacuable

5   enclosure for carrying out substrate processing. The chamber body 458 has a plurality of

ports including at least a substrate entry port that is selectively sealed by a slit valve and a

side port through which a substrate support member can move. The apparatus 400 also

includes a vapor precursor injector 446 connected to the chamber 402, and a liquid

precursor injector 442 connected to the chamber 402.

10   In the liquid precursor injector 442, a precursor 460 is placed in a sealed container

461. An inert gas 462, such as argon, is injected into the container 461 through a tube

463 to increase the pressure in the container 461 to cause the liquid precursor 460 to flow

through a tube 464 when a valve 465 is opened. The liquid precursor 460 is metered by a

liquid mass flow controller 466 and flows into a tube 467 and into a vaporizer 468, which

15   is attached to the CVD or NLD chamber 402. The vaporizer 468 heats the liquid causing

the precursor 460 to vaporize into a gas 469 and flow over a substrate 483, which is

heated to an appropriate temperature by a susceptor to cause the vaporized precursor 460

to decompose and deposit a layer on the substrate 483. The chamber 402 is sealed from

the atmosphere with exhaust pumping 475 and allows the deposition to occur in a

20   controlled partial vacuum.

In the vapor precursor injector 446, a liquid precursor 488 is contained in a sealed

container 489 which is surrounded by a temperature controlled jacket 423 and allows the

precursor temperature to be controlled to within 0.1°C. A thermocouple (not shown) is

immersed in the precursor 488 and an electronic control circuit (not shown) controls the

25   temperature of the jacket 423, which controls the temperature of the liquid precursor and

thereby controls the precursor vapor pressure. The liquid precursor can be either heated

or cooled to provide the proper vapor pressure required for a particular deposition

5   process. A carrier gas 480 is allowed to flow through a gas mass flow controller 482, when valve 457 and either valve 492 or valve 495, but not both, is opened. Also shown is one or more additional gas mass flow controllers 486 to allow additional gases 484 to also flow when valve 487 is opened, if desired. Additional gases 497 can also be injected into the vaporizer 468 through an inlet tube 498 attached to valve 479, which is attached

10   to a gas mass flow controller 499. Depending on its vapor pressure, a certain amount of precursor 488 will be carried by the carrier gases 480 and 484, and exhausted through tube 493 when valve 492 is open.

       After the substrate has been placed into the chamber 402, it is heated by a heater as discussed above. After the substrate has reached an appropriate temperature, valve

15   492 is closed and valve 495 is opened, allowing the carrier gases 480 and 484 and the precursor vapor to enter the vaporizer 468 through the attached tube 496. Once the precursor 488 is vaporized, it is carried through the mass flow controller 491. Such a valve arrangement prevents a burst of vapor into the chamber 402. A vapor distribution system, such as a shower head 468 or a distribution ring (not shown), is used to evenly

20   distribute the precursor vapor over the substrate 483. After a predetermined time, depending on the deposition rate and the thickness required for the initial film deposition, valve 495 is closed and valve 492 is opened. The flow rate of the carrier gas can be accurately controlled to as little as 1 sccm per minute and the vapor pressure of the precursor can be reduced to a fraction of an atmosphere by cooling the precursor 488.

25   Such an arrangement allows for accurately controlling the deposition rate to less than 10 angstroms per minute, if so desired.

5   Figs. 7A-7B show two operating conditions of an embodiment 500 to perform

high pressure barrier pulsed plasma atomic layer deposition. Fig. 7A shows the

embodiment 500 in a deposition condition, while Fig. 7B shows the embodiment 500 in a

rest condition. Referring now to Figs. 7A-7B, a chamber 502 receives gases through one

or more gas inlets 467, 496, 498, as shown in Figure 6. A solid state plasma generator

10   510 is mounted on top of the chamber 502 and one or more plasma excitation coils 570

are positioned near the gas inlets 568. A liquid precursor system 542 introduces

precursor gases through a vaporizer 568 into the chamber 502 using a precursor

distribution ring 568 (see also 469 in Figure 6).

A chuck 503 movably supports a substrate 583. In Fig. 6A, the chuck 503 and the

15   substrate 583 are elevated and ready for deposition. The substrate 583 is positioned

inside the chamber. Suitable processing gas is introduced into the chamber through the

inlets 568, and a pulsed plasma controller 510 is periodically turned on in accordance

with a process activation switch to drive the desired process. The particular type of

process to be performed affects the process activation switch choice. The choice of

20   activation switch for any device fabrication process, regardless of whether the process is

a deposition or etch process, also may significantly affect the final semiconductor device

properties. At the conclusion of the processing of one layer of material, the gas in the

chamber 502 is purged, and the chamber 502 is ready to accept further processing. This

process is repeated for each layer in the multi-layer wafer. At the conclusion of

25   deposition of all layers, the chuck 503 is lowered and the substrate 583 can be removed

through an opening 511.

The system allows the substrates to have temperature uniformity through reliable real-time, multi-point temperature measurements in a closed-loop temperature control. The control portion is implemented in a computer program executed on a programmable computer having a processor, a data storage system, volatile and non-volatile memory and/or storage elements, at least one input device, and at least one output device.

Each computer program is tangibly stored in a machine-readable storage medium or device (e.g., program memory or readable disk) readable by a general or special purpose programmable computer, for configuring and controlling operation of a computer when the storage media or device is read by the computer to perform the processes described herein. The invention may also be considered to be embodied in a computer-readable storage medium, configured with a computer program, where the storage medium so configured causes a computer to operate in a specific and predefined manner to perform the functions described herein.

The results of one experimental run are discussed next. First, an exemplary process recipe for depositing titanium nitride is detailed below:

Process	step	time	function	Pressure(T)	carrier	liquid	N_2	plasma	H_2	chuck
Pre-clean	1	4s	Pump	0	0	0	0	0	0	up
	2	3s	Strike	0	0	0	5	1200	0	up
	3	15s	Plasma	0.4	100	0	5	1200	0	up
deposition	4	10s	Stab	1.5	100	10	0	0	0	up
	5	6s	dep1	1.5	100	10	0	0	0	up
	6	3s	Purge	0	100	0	0	0	0	up
	7	3s	Pump	0	0	0	0	0	0	up
	8	3s	Strike	0	0	0	5	1200	0	up
	9	30s	plasma1	0.4	100	0	5	1200	0	up
	10		loop to step 4 (stab)							
Cooling	11	1s	Plasma off	0	100	0	0	0	0	up
	12	30s	Cool	0	100	0	0	0	0	down

5   Steps 1-3 relate to pre-cleaning of the substrate surface. In these steps, the

chamber is brought to a low pressure by evacuation pumping for 4 seconds. Next, the

plasma is struck for 3 seconds. The strike operation allows the plasma to be started at

low pressure and then the plasma is turned on for 15 seconds at a higher pressure. The

plasma is turned on at a pressure of 0.4 Torr to provide high pressure, high density

10   plasma for isotropic surface conditioning.

After pre-cleaning, the flow and pressure is stabilized for 10 seconds. A first

deposition step is performed for 6 seconds. The chamber is purged with carrier gas or an

inert gas such as N_2 for 3 seconds, and the valve to the pump is open for 3 seconds to

remove all liquid precursors and/or vapor residues in the chamber. A plasma strike

15   operation is performed for 3 seconds, and plasma treatment for the first deposition is

activated for 30 seconds at a pressure of 0.4 Torr. For each additional deposition, the

process loops back to step 4. When the wafer deposition is complete, the plasma is

turned off for one second and the substrate is optionally cooled down for 30 seconds

before it is removed from the chamber. The timing of the steps are illustrative and can be

20   varied from as low as a half a second to as high as five minutes, depending on the desired

property of the film and the film quality, among others.

Fig. 8 shows a flow chart of a nanolayer thick film process in accordance with one

embodiment of the invention. NLD technique is a combination of ALD and CVD and

thus makes use of the advantages of both ALD and CVD. The process of Fig. 8 includes

25   evacuating a chamber of gases (step 602); exposing a device to a gaseous first reactant,

wherein the first reactant deposits on the device to form the thin film (step 604); purging

the chamber and evacuating the chamber of gases (step 606); and exposing the device,

5   coated with the first reactant, to a gaseous second reactant under plasma, wherein the thin

film deposited by the first reactant is treated to form the same materials or a different

material (step 608). The process can be repeated if the decision to continue (step 610) is

made. Alternatively, the process can be terminated (step 612).

In one embodiment of the process of Figure 8, a first gas reactant is flowed over a

10   wafer surface and deposits on the wafer. The amount of the first gas reactant into the

chamber is controlled by a liquid flow controller ("LFC") and valves to control the

deposition of a layer that is more than a monolayer thick to a few nanometers thick. The

first reactant can then be purged with inert gas, and pumped. A second reactant is flowed

into the chamber to react with the first reactant to form a layer that is more than a

15   monolayer thick to a few nanometers thick. A high density plasma may be used during

the second reactant injection to enhance or maintain the conformality of the deposited

film on complex topography. The density of the deposited film may also increase after

the high density plasma treatment during the second reactant injection. The second

reactant then is optionally purged and removed by pumping. Other reactants can be

20   flown in to react with deposited and reacted film to form a final film. The above steps

are repeated to form a thick film that is a multiple in thickness of the layer that is more

than a monolayer thick to a few nanometer thick. The thickness of each repeat or cycle

deposited thus is more than a monolayer thick, but the subsequent reactants under high

density plasma can still react with the full thickness of the deposited film to achieve a

25   high quality and uniform film.

For the above NLD process, the materials deposit on the wafer in the deposition

temperature regime and not by adsorption. The temperature in some cases is higher than

5   the temperature of the ALD process, but lower than that of the conventional CVD process

and adequate for other semiconductor processes. Since the NLD process is a deposition

process rather than a self-limiting surface adsorption reaction process, the deposition rate

to achieve a thickness of more than a monolayer to a few nanometers is controlled by an

LFC and valves. The deposition rate in NLD process can also be controlled by tailoring

10   the wafer temperature or chuck (or susceptor) temperature, process pressure, and gas flow

rate, among others.

The process of deposition of nanolayer thick film provides almost completely

conformal deposition on complex topography as that in semiconductor devices having 0.1

micron width with an aspect ratio of more than 8:1. Excellent conformality of film is

15   achieved with NLD similar to that of ALD, and far superior than conformality of thick

CVD film.

Where a film of a few to 10 nanometers thick is required, the NLD process

provides higher throughput, since in each NLD cycle, a film of more than a monolayer to

a few nanometers thick film is deposited. Since the NLD process has high throughput,

20   the minimal volume constraint as in the ALD process is not necessary, and a

conventional CVD chamber can be used to achieve highly conformal, high quality, high

throughput films.

Since a film of more than a monolayer to a few nanometers thick is deposited in

each cycle, the microstructure of the resulting film can be of nanocrystalline structure in

25   an amorphous matrix, which can be ideal for certain applications, such as diffusion

barrier for copper.

5   Since NLD is a deposition process, the precursors or gases are not limited to only those that deposit by a self-limiting surface reaction. NLD thus is not limited to ALD precursors and can be used to deposit a vast number of film materials from currently available precursors.

Figure 9 shows a Transmission Electron Micrograph ("TEM") of a structure that

10   is deposited with a thin film in accordance with the steps discussed above. The structure has a height of approximately 800 nm, and an average width of approximately 90 nm. The aspect ratio of the structure is thus more than 8:1. Also seen in the Figure is 9 nm thin film of TiN that is deposited film in accordance with the steps discussed above onto the structure from the top. As shown therein, the thickness of the deposited film is

15   approximately the same on top, on the sidewalls, and on the bottom of the structure, within the measurement approximation. Close examination of the micrograph indicates that the conformality of the deposited film is close to 100 %. In comparison, conventional deposition methods using low density plasma – capacitance-coupled plasma typically results in a directional, non-isotropic bombardment of plasma treatment,

20   resulting in non-treatment of the sidewalls.

Figure 10 shows a plot of film resistance increase of the titanium nitride ("TiN") thin films as a function of time for the above process. The demonstrated TiN film was deposited using TDMAT precursor and N_2 flow under plasma treatment in accordance with the steps discussed above. The wafer temperature during deposition was

25   approximately 325 C°. The resistivity of the bulk film is approximately 300 µOhm-cm. As shown therein, the sheet resistance increases approximately 4.2% for sample 1, which has a thickness of approximately 10 nm, approximately 3.5% for sample 2, which has a

5   thickness of approximately 20 nm, and less than 2% for sample 3, which has a thickness

of approximately 60 nm, over a period of approximately twenty four hours. The plot

shows that the film is stable with minor resistance fluctuations. The increase in

resistance in these TiN films deposited with a thin film following the steps disclosed

above is significantly lower than reported values. K.C. Park et al. reported a 100 nm

10   thick TiN film deposited using TDMAT precursor in an N_2 ion-beam-induced plasma

CVD system increases almost 10% in resistivity after 24-hour air exposure. The

conformality of the films also degrades to below 5%, in contrast to almost 100%

conformality achieved with the film deposited in accordance with the steps discussed

above. The advantage of using TDMAT precursor for TiN deposition is the lower

15   deposition temperature compared to other precursors such as $TiCl_4$ and NH_3 which

require a deposition temperature of higher than 600 degrees Celsius for good quality TiN

film. Thermal TDMAT and TDEAT process produce highly conformal TiN films but

with high carbon contamination, high resistivity of more than 2000 µOhm-cm, and

unstable after air-exposure. Reactions of these films with NH_3 in various plasma reduce

20   the impurities and resistivity; the conformality, however, is also degraded. Nitrogen

plasma treatments also have been studied with TDMAT precursor. In general, however,

conventional deposition methods using low density plasma - capacitance coupled plasma

in down-stream or parallel plate configuration typically result in a directional, non-

isotropic bombardment of plasma treatment, resulting in non-treatment of the sidewalls.

25   More details on TiN deposition using different precursors and plasma treatments are

discussed in K.C. Park et al., the content of which is incorporated by reference.

5   It should be realized that the above examples represent a few of a virtually

unlimited number of applications of the plasma processing techniques embodied within

the scope of the present invention. Furthermore, although the invention has been

described with reference to the above specific embodiments, this description is not to be

construed in a limiting sense. For example, the duty ratio, cycle time and other

10   parameters and conditions may be changed to obtain desired wafer characteristics.

Various modifications of the disclosed embodiment, as well as alternative

embodiments of the invention, will become apparent to persons skilled in the art upon

reference to the above description. The invention, however, is not limited to the

embodiment depicted and described. For instance, the radiation source can be a radio

15   frequency heater rather than a lamp. Hence, the scope of the invention is defined by the

claims that follow. It is further contemplated that the claims will cover such

modifications that fall within the true scope of the invention.